



Effect of filler type on crystallinity of low-density polyethylene composites

Iji, Martins.^{a*}, Abba Hamza.^b, Okpanachi, Clifford.^c

^a Department of Chemistry, Abubakar Tafawa Balewa University, P.M.B. 0248, Bauchi, Nigeria

^b Department of Chemistry, Ahmadu Bello University, P.M.B.1045, Zaria-810006, Nigeria.

^c Department of Pure and Industrial Chemistry, Kogi State University, P.M.B 1008, Anyigba.

ARTICLE INFO

Article history:

Received
Received in revised form
Accepted
Available online

Keywords:

Coumarin
Potassium 2-oxoimidazolidine-1,3-diide
Multicomponent reaction
4-hydroxycoumarin

ABSTRACT

In this study, crystallinity was investigated for Low-Density Polyethylene composites of bagasse and sweet potato peel (SPP) compounded with an internal mixer as compared to the pure low-density polyethylene that acted as the control sample. This investigation was carried out for total filler content of 30% by weight of the composites for three types of composites being; bagasse-filled, SPP-filled and hybrid composites of Low-Density Polyethylene filled with both bagasse and SPP. XRD analysis showed a decrease in the degree of crystallinity of the composites as compared to the pure Low-Density Polyethylene. This is a general trend with composites where the introduction of fillers brings about a reduction in the crystallinity of polymer materials. The bagasse composite, sweet potato peel composite and the hybrid composites had degrees of crystallinity of 33.25%, 33.15% and 34.15% respectively, as against that of the pure LDPE which was 36.41%.

1. Introduction

Over the years, with the boost in manufacturing and other industrial activities such as transportation (aerospace, aircraft, marine, automotive), construction and numerous other industrial and consumer applications, there has become a continuous expansion in the market for polymer composites. This increased application of composites in place of conventional materials is driven by their proven advantages such as corrosion resistance, high strength-to-weight ratio, and moderate costs as well as the design flexibility offered by novel resin/reinforcement combinations together with new processing and machinery innovations [1].

The growing concern of resource depletion and environmental pollution posing a serious challenge to engineers and scientists in the world, the need arises to develop new materials that rely on renewable sources. This has led to research of biocomposite materials [1].

Every year, 125 million tons of plastic are produced in the world, which 42% of the consumption of plastics is in the packaging industry and 47% of it is related to food packaging [7]. Petroleum polymers (plastics) have some good characteristics, including low cost, good printing, easy plasticity and high chemical resistance, which cause

to the increasing application of these polymers. But plastics are not renewable, causing enormous contamination of the environment and causing a lot of biological problems. Therefore, researchers are trying to replace these polymers with biodegradable (biocomposite) polymers in order to reduce environmental pollutions. Biodegradable polymers are less energy-consuming than plastics. Biodegradable polymers are converted into water-soluble polymers due to the degradation of functional groups such as the ester and amide bonds in their chemical structure [8-9]. Biocomposites are made of a polymer, serving as a matrix and cellulose material which acts as the reinforcing filler [2]. Biodegradable polymers are a special type of polymer that decompose after their intended purpose by the process of bacterial decomposition with the formation of by-products such as CO₂, N₂, water, and mineral salts. These polymers are made naturally and artificially and are mainly composed of ester, amide and ether agents [6].

The reinforcement of linear and cross-linked polymers is a process of their compatibilization with various solid, liquid, and gaseous substances which are uniformly distributed in the bulk of polymer and have a pronounced phase border with polymeric phase (matrix). Polymers filled with solid particulate or fibrous fillers of

* Corresponding author. e-mail: martinsiji247@gmail.com

organic and inorganic nature are classified as polymeric composite materials. Polymeric composite materials have been known since ancient times. Some of the earliest composites were layers of fiber, cloth, and pitch. All these materials have the same common physico-chemical feature.

The reinforcement of linear and cross-linked polymers is a process of their compatibilization with various solid, liquid, and gaseous substances which are uniformly distributed in the bulk of polymer and have a pronounced phase border with polymeric phase (matrix). Polymers filled with solid particulate or fibrous fillers of organic and inorganic nature are classified as polymeric composite materials. Polymeric composite materials have been known since ancient times. Some of the earliest composites were layers of fiber, cloth, and pitch. All these materials have the same common physico-chemical feature. They are heterophasic (consisting of two or more phases) polymer systems in which phases interact with one another. The appearance of new properties is determined not only by proportion of two (or more) different materials but also by the interphase phenomena [3].

As a result, polymers, thermoplastics and thermosets, can be reinforced to produce quite frequently a completely new kind of structural materials [4].

Bagasse is the residue fiber remaining after the extraction of sugar from sugar cane. It is composed of thick-walled, long fiber and pith [5]. Bagasse is a plentiful lignocellulosic waste typically found in tropical countries that process sugar cane, such as Brazil, India, Cuba, China and Nigeria [5].

Sweet potato (*Ipomoea batatas*) is a dicotyledonous plant that belongs to the family *Convolvulaceae*. Its large, starchy, sweet-tasting, tuberous roots are a root vegetable [10]. In 2011, about 106.5 million tons of sweet potatoes were estimated to have been cultivated according to Food and Agriculture Organization of the United Nations. In the same year, about 2.8 million tons were produced in Nigeria [11].

X-ray diffraction is a technique used to identify preferred orientation, crystalline areas, and grain size of crystalline materials. If the structures are arranged in an orderly array or lattice, the interferences of the electromagnetic radiation of the X-ray with the structure are sharpened so that the radiation is scattered or diffracted only under specific experimental conditions. X-ray diffraction techniques are useful for semi crystalline polymers and reorganization of crystalline phases (polymorphism) of polymers. X-ray diffraction is a primary technique used to determine the degree of crystallinity in polymers because polymers are not 100% crystalline in nature. Chain confirmation is given by XRD. For example, the repeat distance of 2.55 Å in the crystals of polyethylene is readily identified with a single repeat unit in the planar zigzag conformation [12].

2. Results and Discussion

XRD analysis was utilized to establish the effect of the filler on the crystallinity of the polymer composites.

X-ray diffractograms of the pure LDPE, bagasse-filled, SPP-filled and bagasse/SPP-filled composites are shown in Figures 1 – 4.

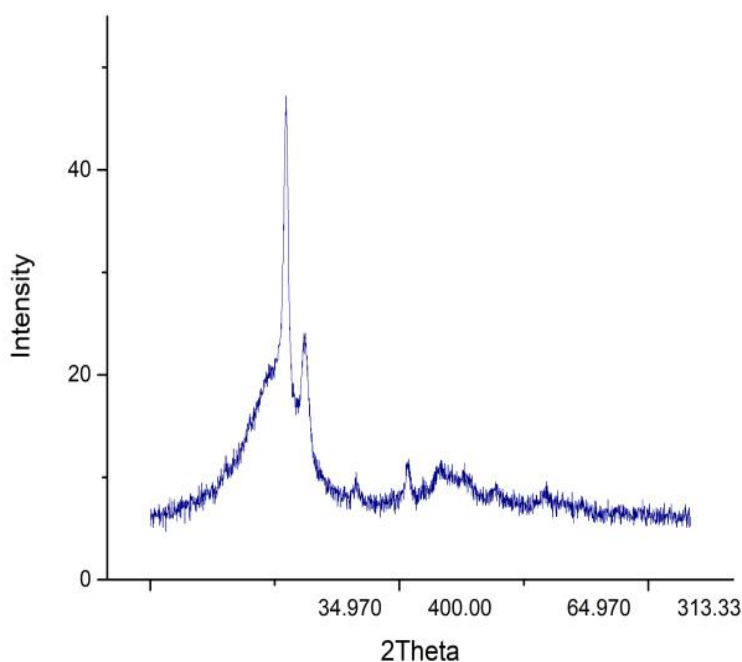


Figure 1: X-ray Diffractogram for 100% LDPE

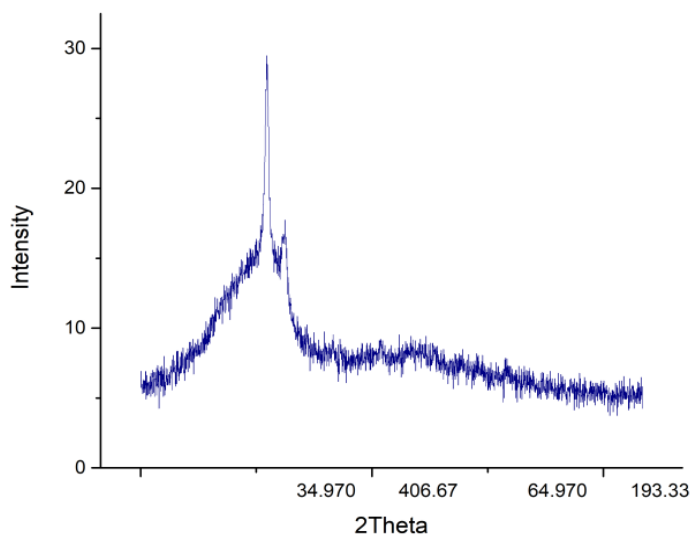


Figure 2: X-ray Diffractogram for Bagasse-filled LDPE Composite.

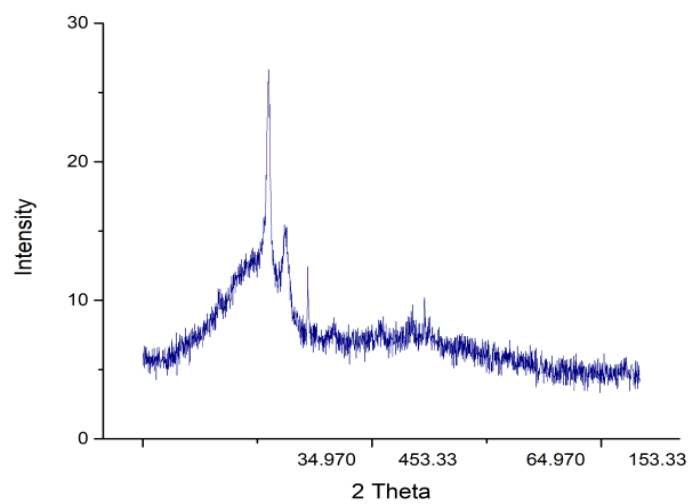


Figure 3: X-ray Diffractogram for SPP-filled LDPE Composite.

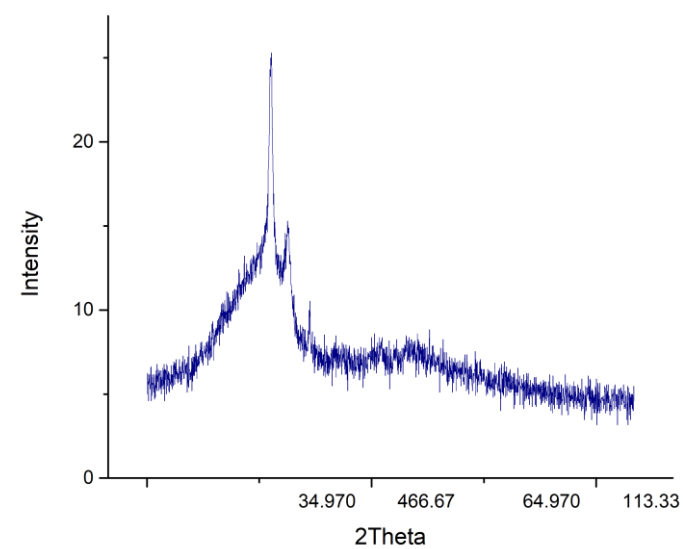


Figure 4: X-ray Diffractogram for Bagasse/SPP-filled LDPE Hybrid Composite.

X-ray diffraction is the primary, non-destructive tool for determining important solid-state structural information such as the degree of crystallinity of semi-crystalline, amorphous polymeric and composite materials.

From these results, the diffractograms for the pure LDPE and the LDPE composites showed regions of crystallinity and amorphism. It can be seen that LDPE and its composites are partly crystalline and partly amorphous as there is the presence of sharp narrow diffraction peaks and broad peak.

The diffractogram for the 100% LDPE exhibited two characteristic peaks at 21.4° and 23.7° 2θ values corresponding to 110 and 200 reflections respectively. Similarly, the diffractogram for the bagasse-filled composite exhibited two characteristic peaks at 21.4° and 23.6° 2θ values corresponding to 110 and 200 reflections respectively. The SPP-filled composite and the bagasse/SPP-filled hybrid composites, on the other hand exhibited three major peaks, the two peaks at 21.4° and 23.6° 2θ values corresponding to 110 and 200 reflections respectively characteristic of LDPE and its composites and a third peak at 26.6° 2θ value corresponding to the 210 reflection.

The 110, 200 and 210 reflections of diffractogram peaks were consistent with the orthorhombic crystal structure of polyethylene and its composites. The diffractograms for the composites displayed some differences in patterns as compared to the pure LDPE. There was observed decrease in d-spacing of the composites, compared to the pure LDPE. Another observation was the decreased intensity of peaks in the diffractograms of the composites, compared to the pure LDPE, for example, the prominent peak at 21.4° 2θ value had an intensity of around 12000 in the pure LDPE but had 4000, 3800 and 3000 for the bagasse, SPP and hybrid composites respectively. This points to a lowering of the crystalline nature of the polymeric materials with the introduction of the fillers.

The crystallinity index of the materials as estimated by comparing the areas of the peaks due to the crystalline phases with the areas due to the amorphous phases showed that of the pure LDPE to be higher, at 36.41%, than those of the bagasse, SPP and hybrid composites which displayed crystallinity indices of 33.25%, 33.15% and 34.15% respectively. This suggests, unsurprisingly that the introduction of the fibrous fillers brought about a noticeable reduction in the crystallinity of the polymer.

On comparing the crystallinities of the heterophasic composites, the hybrid composite of bagasse and SPP showed a higher degree of crystallinity than the bagasse and SPP composites. This may be due to a combined effect of the three systems.

3. Experimental

3.1. General

The low density polyethylene (LDPE) used as the matrix material in this research was manufactured by Indorama Eleme Petrochemicals Ltd Nigeria as pellets with specific gravity and density 0.95 and 0.92 g/cm^3 respectively.

Bagasse was gotten from sugarcane obtained from the Samaru market in Zaria, Kaduna state, Nigeria for purpose of this research. The sugarcane was purchased and the juice was extracted, leaving the bagasse. The sweet potato peel used for this research was obtained by peeling of potatoes purchased from the Samaru market in Zaria, Kaduna state, Nigeria. XRD data were collected using an ARL X'TRA model X-ray diffractometer, serial number 197492086, equipped with Cu radiation source (wavelength $\lambda = 1.540562 \text{ \AA}$) operating at 40 kV and 40 mA and a Vantec detector.

3.2. Alkalization treatment of fillers

The bagasse and sweet potato peel fillers used for this research were alkalized by first soaking in water to get rid of sand and other impurities and then dried in the sun before being transferred to an oven at 70°C , for 12 hours. The filler fiber was then immersed in 1% sodium hydroxide solution for 3 hours at room temperature, thoroughly washed with deionised water and air-dried.

3.3. Crushing of fillers

After alkalization, the fillers were ball milled at 200 rpm for 6 hours and then sieved with a $450 \mu\text{m}$ sieves for 15 minutes to obtain uniform particle size of fillers according to ASTM D1921 [13].

3.4. Preparation of the Composite

In accordance with ASTM D4976 standard method [14], the composites were prepared by the thermal mixing procedure, with an internal mixer at 180°C and rotor speed of 50 rpm for 8 minutes. This was following by hot pressing at 180°C for 10 minutes before the mixture was cooled at room temperature of 30°C for 15 minutes.

3.5. X-Ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) was used for phase identification and determination of degree of crystallinity of the composites. The specimen was prepared for XRD by side loading. The XRD pattern of the samples were recorded over the angular range $2\theta = 5 - 70^\circ$ at a temperature of 25°C with a count time of 189.5 second per step and a step size of 0.03° . The sample was held firmly on the specimen holder and placed in the diffractometer and the diffractogram collected on a computer screen. The collected data from X-ray diffractometer were processed using Origin Pro-8 to obtain information on the phase identification and crystalline morphology of the composites. Plots of intensity against 2θ were obtained for each sample and the degree of crystallinity was determined using prominent peaks in each diffractogram plotted.

4. Conclusion

This study has presented the effect of different composite systems of low density polyethylene (LDPE) with bagasse and sweet potato peel fillers as a factor that affects the crystallinity of the composites of the polymer. The introduction of the lignocellulosic fillers in the composite system is shown to decrease the degree of crystallinity of the material. This is in tandem with the work of Xin et al., who studied the influences of carbon fillers on electrical conductivity and crystallinity of polyethylene terephthalate. They recorded that the crystallinity of PET decreased with increasing the filler content in the composites and all types of fillers caused shifting of the crystallization temperature to higher temperatures [15]. The highest crystalline index of the composites was obtained for the hybrid composite. This supports the claim by Guo et al., that fiber/matrix interface of fiber play key roles for the crystallization behavior of composites and has a close relationship with the properties of the industrial product reinforced with natural protein fiber, having studied the influence of interface and thermal conductivity of filler on the nonisothermal crystallization kinetics of polypropylene/natural protein fiber composites [16].

Acknowledgements

Our sincere gratitude is expressed to Prof. Paul Mamza for his continuous support, advice, insightful criticisms and patient encouragement throughout the time of this research. Technical support by Samuel Ndaghiya Adawara of the Department of Pure and Applied Chemistry, University of Maiduguri, Borno, Nigeria is also immensely acknowledged and appreciated.

References

[1] Ofem, M.I., Abam, F.I. and Ugot, I.U. (2012). Mechanical Properties of Hybrid Periwinkle and Rice Husk Filled CNSL Composite. *International Journal of Nano and Material Sciences*, 1(2): 74-80.

[2] Obasi, H.C. (2012). Studies on Biodegradability and Mechanical Properties of High Density Polyethylene/Corncob Flour Based Composites, *International Journal of Scientific & Engineering Research* Vol. 3, Iss 8, pp.1-4.

[3] Lipatov YS. (1995). Polymer reinforcement. ChemTec publishing, Ontario, Canada, pp. 1.

[4] Ebewe, R. O. (2000). *Polymer Science and Technology*. CRC Press LLC, Boca Raton New York, 238-240.

[5] Aigbodion, V.S., Hassan, S.B., Ause, T. and Nyior, G.B. (2010). Potential utilization of solid waste (Bagasse Ash).

Journal of Minerals & Materials Characterization Engineering, 9, 67-77.

[6] Pirs, S., Mohtaramia, F. and Kalantari, S. (2020) Preparation of biodegradable composite starch/tragacanth gum/Nanoclay film and study of its physicochemical and mechanical properties. *Chemical Review and Letters*, 3(3), pp.98-103.

[7] Nkwachukwu, O. I., Chima, H. C., Ikenna, A. O. and Alber, L. (2013). Focus on potential environmental issues on plastic world towards a sustainable plastic recycling in developing countries. *International Journal of Industrial Chemistry*, 4, pp. 1-34.

[8] J. H. Han, Edible films and coatings: A review. *Innovations in Food Packaging*, 2, (2014) pp. 213-255.

[9] A. M. Youssef and S. M. El-Sayed, Bionanocomposites materials for food packaging applications: Concepts and future outlook. *Carbohydrate Polymers*, 193, (2018) pp. 19-27.

[10] Hartemink, A.E., Poloma, S., Maino, M., Powell, K.S., Egenae, J. and O'Sullivan, J.N. (2000). Yield decline of sweet potato in the humid lowlands of Papua New Guinea. *Agriculture Ecosystems & Environment* 79 (2-3): 259.

[11] Danladi, A. and Salihu, I. (2014). Production and Properties of Sweet Potato Flour/High Density Polyethylene Composites. *International Journal of Emerging Technology and Advanced Engineering*. Volume 4, Issue 9, 1-3.

[12] Noorunnisa P. K. and Mariam A. A. (2015). Processing and characterization of polyethylene-based composites. *Advanced Manufacturing: Polymer & Composites Science*.

[13] ASTM D1921, (2012). Standard Test Methods for Particle Size (Sieve Analysis) of Plastic Materials. ASTM International, West Conshohocken, PA.

[14] ASTM D4976, (2004). Standard Specification for Polyethylene Plastics Molding and Extrusion Materials. ASTM International, West Conshohocken, PA.

[15] Xin, F., Li, L., Chan, S. H., & Zhao, J. (2012). Influences of carbon fillers on electrical conductivity and crystallinity of polyethylene terephthalate. *Journal of composite materials*, 46(9), 1091-1099.

[16] Guo, L., Chen, F., Zhou, Y., Liu, X., & Xu, W. (2015). The influence of interface and thermal conductivity of filler on the nonisothermal crystallization kinetics of polypropylene/natural protein fiber composites. *Composites Part B: Engineering*, 68, 300-309.

[17] Guo, L., Chen, F., Zhou, Y., Liu, X., & Xu, W. (2015). The influence of interface and thermal conductivity of filler on the nonisothermal crystallization kinetics of polypropylene/natural protein fiber composites. *Composites Part B: Engineering*, 68, 300-309.

How to Cite This Article

Martins Iji; Hamza Abba; Clifford Okpanachi. "Effect of filler type on crystallinity of low-density polyethylene composites". *Journal of Chemistry Letters*, 1, 4, 2020, 155-159. doi: 10.22034/jchemlett.2021.271721.1018